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Synthesis and Study of Cerium(IV) Polytungstate Nanolayers

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Abstract—For the first time the conditions for the synthesis of cerium(IV) polytungstate nanolayers on the silicon surface by the method of ion layering were defined. The layers were studied by scanning electron microscopy, X-ray microanalysis and transmission FT–IR spectroscopy. The synthetized layer is shown to have a globular structure with the size of the globules in the range of 30–50 nm, with the ratio of cerium/tungsten atomic concentrations equal to 0.8.

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Synthesis of nanolayers and nanostructures by the layer-by-layer technique using solutions of reagents is known to be increasingly used to create new nanomaterials. The results of studies in this field are summarized in the monograph [1] and reviews, e.g., [2–5], which contain the data on the syntheses with the use of molecules, ions, and colloidal particles as reactants.

The purpose of this study was the layer-by-layer synthesis by ion layer deposition (ILD) of the cerium(IV) polytunstate nanolayers. Such a compound may be a promising functional material with a new set of photochromic, catalytic, and sorption properties. In recent years much attention was paid to the study of thin-film structures containing tungsten oxide and cerium [6–11].

The synthesized layer, as follows from the FT–IR spectrum (Fig. 1) is characterized by absorption bands with peaks at 3400 and 1626 cm^{-1} related respectively to the stretching and bending vibrations of water molecules in the layer, as well as the absorption bands at 3225 cm^{-1} and 3070 cm^{-1} of stretching and at 1437 cm^{-1} of bending vibrations of NH bonds in the NH_4^+ cation. It is noteworthy that a strong absorption bands with peaks at 938 and 828 cm^{-1} can be attributed to the W=O and WOW stretching vibrations, respectively, in the polytungstate anion. As to a broad absorption band in the range 750–500 cm^{-1}, it should according to [12] include stretching vibrations of the Ce–O bonds. After heating at 200°C the absorption related to water molecules and ammonium ions disappeared from the spectrum of the sample.

As follows from X-ray spectral microanalysis (Fig. 2), the composition of the layer includes the atoms of cerium, tungsten, and oxygen. Quantitative treatment gives the cerium/tungsten concentration ratio equal to 0.8. The concentration of oxygen in the layer was not determined because it was impossible to identify the oxygen peak intensity in the layer on the background of the general peak of oxygen in the

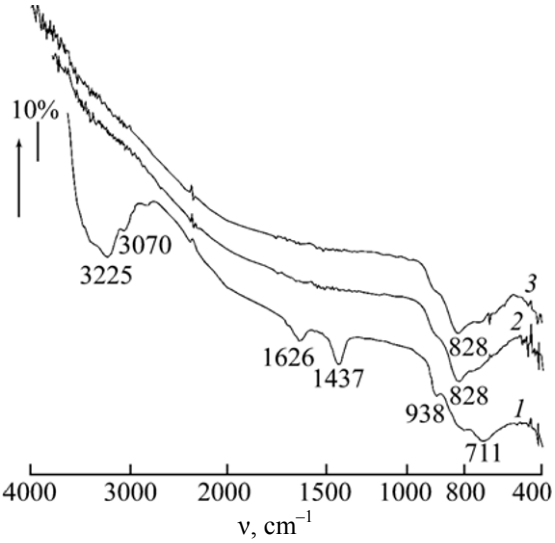

Fig. 1. FT–IR transmission spectrum of a cerium(IV) polytunstate layer synthesized on the surface of silicon single crystal in 25 cycles of ion layer deposition: (*1*) initial sample, (*2*) and (*3*) the sample heated in air for 0.5 h at 200 and 400ºC, respectively.

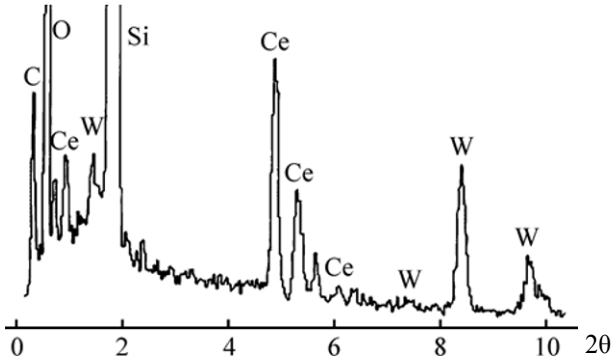

Fig. 2. Energy dispersive X-ray spectrum of the cerium(IV) polytunstate layer synthesized on the silicon surface in 25 cycles.

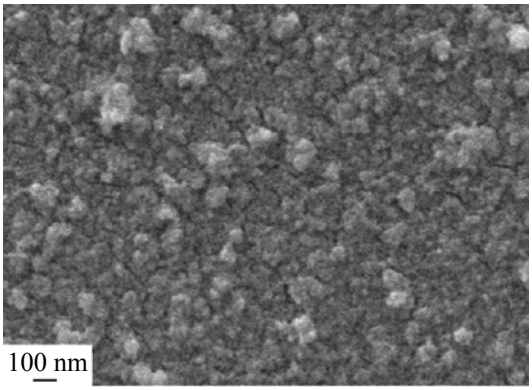

Fig. 3. The scanning electron microscopy image of the surface of cerium(IV) polytunstate layer synthesized on the silicon surface in 25 cycles of ion layer deposition.

structure that includes a layer of synthesized silicon oxide, a layer of silicon oxide on silicon, and silicon. Quantitative determination of nitrogen in the layer also was not performed due to proximity of the peaks to be analyzed.

According to the data of scanning electron microscopy, the synthesized layer has a uniform globular structure with the globule size in the range of 30–50 nm (Fig. 3).

The analysis of the experimental data obtained allows us to construct the following scheme of reactions occurring on the substrate surface during the synthesis. In the first step of the reaction, at processing the substrate with a solution of $(NH_4)_2Ce(NO_3)_6$, the cerium(IV) cations are adsorbed on the surface of the layer of silicon oxide on silicon, and the surface acquires a positive charge. At further processing with a solution of ammonium tungstate, the surface adsorbs negatively charged anion $W_{12}O_{39}^{6-}$ and becomes negatively charged again, so that there is an opportunity for the adsorption of cerium cations in the next cycle of ion layer deposition. The sequential and multiple treatment of the substrate with these reagents leads to the formation of the surface layer including a tungstate polyanion and cerium(IV) cations in its composition.

Thus, for the first time the possibility of synthesizing nanolayers using ion layer deposition of cerium(IV) polytunstate was experimentally demonstrated.

EXPERIMENTAL

The FT–IR spectra were recorded on a Perkin-Elmer 1760X spectrophotometer, 20 scans. Electron micrographs were obtained using a Zeiss EVO-40EP scanning electron microscope with LaB_6 cathode operated at the accelerating voltage of 20 keV. Determination of the composition of the synthesized layer was carried out using an Oxford INCA 350 energy dispersive analyzer with a Si(Li) detector of 30 mm^2 active area.

The substrates for the synthesis of nanolayers were silicon KDB-40 wafers of <100> orientation, polished to 14 class. Before the synthesis, the substrates were rinsed with acetone to remove organic contaminants, with diluted (1:10) hydrofluoric acid and water. After that, for the formation of oxidized hydroxylated surface they were kept for 0.5 h in a "piranha" solution, which is a mixture of 30% H_2O_2 and concentrated H_2SO_4 (volume ratio 3:7), then washed with water, soaked for 0.5 hours in a pH 9 KOH solution and washed again with water.

The reagents were the salts $(NH_4)_2Ce(NO_3)_6$ and $(NH_4)_2WO_4$ of reagent grade, production of Vekton (Russia). For the synthesis was used 0.01 M solution of $(NH_4)_2Ce(NO_3)_6$ with the equilibrium pH = 2.4. To prepare the polytungstate solution a weighed sample of $(NH_4)_2WO_4$ was dissolved in 50 ml of distilled water and then while vigorous stirring the concentrated nitric acid was added to pH = 2.5. At this pH value, according to [15], the anions in the ammonium tungstate solution are in the form of polyoxotungstate $W_{12}O_{39}^{6-}$. The time between preparing the solution and the synthesis was no less than 2 h. After the standard treatment the substrates were mounted in holders for samples of an automated computer-controlled systems for the synthesis and were treated by dipping in succession into solutions according to a certain scheme, to form an elementary ionic layer deposition

cycle: $(NH_4)_2Ce(NO_3)_6$ solution, washing liquid, a solution of ammonium tungstate, again washing liquid. The time of processing the sample with each reagent was 0.5 min. As a result of such sequence of treatments, a nanolayer formed on the surface of the substrate. Synthesis of the subsequent layers was carried out by repeating the cycles.

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